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VISIBLE ABSORPTION SPECTRUM OF BENZOQUINONE*

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Plate X A & B and XI

ABSTRACT. The visible absorption spectrum of *p*-benzoquinone was studied in the vapour state The bands which lie in the region of 4100-5000 Å consist of eight main groups developed at 100°C in a 50 cm cell About 175 bands are measured in this region. These bands are very sharp, many of them having double and triple heads. One marked feature is the appearance of companion bands with separations of 36 cm^{-1} lying on the shorter wave-length side. An analysis has been proposed assigning the bands as due to $n-\pi(Au \leftarrow Ag)$ transition.

INTRODUCTION

Benzoquinone ($C_6H_4O_2$) is an important organic compound. It is a forerunner of many dyes as well as anti-biotics. The spectra of its solution enabled Braude (1945) to recognise three different band systems, two in the ultra-violet and one in the visible region.

Benzoquinone molecule which belongs to symmetry group D_{2h} is to be distinguished from other para-substituted benzene molecules in an important way. In the former the π-electrons are no longer mobile over the entire framework of the molecule with the result that bonds become localised. With a view to understand the bearing of this structural difference on the spectra of the molecule, the absorption spectra of benzoquinone in its vapour state were investigated in detail. The spectrum of the vapour consists of the three band systems (Asundi and Singh, 1955), two in the ultraviolet region and one in the visible region as already recognised by Braude in its absorption spectrum of the solution. The two ultraviolet systems are reported elsewhere In general, they do not correspond to the band systems of di-substituted benzenes in the same region. The present paper deals with the analysis and discussion of the visible system of bands.

EXPERIMENTAL

The spectrograms were obtained with a quartz Hilger E492 spectrograph and a three prism 'Steinheil' glass spectrograph was used for the visible region. The dispersion of the former is about 17Å/mm in this region, whereas that of the latter is about 11Å/mm.. The previous work was done on the 'Hilger' E492

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spectrograph and, therefore, the use of the Steinheil as the dispersing apparatus proved successful in resolving the multiple heads of many bands. However, a comparison of the spectra obtained from both the apparatus with regard to intensity of the bands and their grouping was found useful. The major portion of the work was, however, completed on the Steinheil glass spectrograph.

Various absorption cells were tried, but those supplied for the present investigation according to the requirements by the Andhra Scientific Company, Muslipatam, India, were found useful. These cells were 5 cm, 10 cm, and 50 cms in length with fused plane glass end-windows. However, the final spectrograms were photographed with a 100 cm cell with sealed plane windows, the furnace in this case being shorter than the length of the cell. The rest of the procedure was exactly the same as for part II of the series, except for the source of continuous radiation. For this, an automobile head lamp of 25 ? running on a regulated constant voltage (8 volts) from a battery was used. A reflector was used to intensity the radiation which was made into a parallel beam with the help of a lens before entering the cell. Another lens was used to condense the emergent beam on the slit of the collimator. The temperature was then raised in successive steps of 10°C as spectra were photographed from room temperature upto 105°C. Exposures of 1 minute to 2 minutes were generally needed for the various bands. The weak longer wave-length bands were measurd in the spectrograms obtained 105°C with two minutes exposure whereas those obtained at 85°C with two minutes exposure were measured for the shorter wave length bands. However, one very weak shorter wavelength group was measured from a spectrogram obtained at 105°C with four minutes exposure.

RESULTS

The substance is a solid at room temperature and sublimes at 115°C. The absorption spectrum of the vapour was studied from room temperature upto 105°C with the different cell-lengths (Asundi and Singh, 1955). The absorption being very weak in the visible region, longer cells were found suitable. With 50 cm. cell there were no absorption bands in the visible region upto 70°C. At temperature of about 80°C seven main groups of the bands are observed. Of these groups, those at 20974 cm^{-1}, 22032 cm^{-1} and 23157 cm^{-1} are strong, the bad at 22032 cm^{-1} being the strongest band of the system. Besides these three groups, the weak band groups are located at 22476 cm^{-1}, 22837 cm^{-1} and 23955 cm^{-1}. When the temperature is gradually increased, it is observed that these seven band groups become more intense, and most of the bands develop double and triple heads. At the same time, additional weak band groups appear at 19673 cm^{-1}, 20160 cm^{-1}, 20352 cm^{-1}, 20683 cm^{-1}, 21410 cm^{-1} and 21771 cm^{-1} filling the whole space between the first two main bands at 20974 cm^{-1} and 22032 cm^{-1} and extending considerably on the longer wave-length side of the first band

group at 20974 cm^{-1}. At the same temperature, very weak bands also develop on the longer wave-length side of all the seven main bands and an additional extremely weak band group develops at 24280 cm^{-1}. Thus, the spectrum becomes more complex at temperatures between 100° and 105°C.

About 175 bands are measured in the visible region including the twenty-eight bands reported by Seshan (1936). Many of the bands are sharp and have double and triple heads having frequency differences of 7 cm^{-1} to 12 cm^{-1} between them. Some of the bands are very sharp and line-like in appearance. Within the eight main groups seven developed at about 80°C and one developed at about 100°C. There are companion bands lying on the shorter wavelength side of the first band of each group and having a separation of 36 cm^{-1}. However, at temperatures between 100°C and 105°C, the companion bands also develop on the longer wavelength side of the main bands with recurring frequency differences of 37 cm^{-1}, 64 cm^{-1} and 92 cm^{-1}. Many of the bands are too weak to be measured.

TABLE I

Wave-length in Å	Wave-numbers in cm^{-1}	Intensity	Separation from (0 0)	Assignment	Remarks
5081.8	19673	ow, s	−1839	$0-3\times613$	The bands from 19673 cm^{-1} to 20097 cm^{-1} were measured and their intensities estimated from a spectrogram taken at a temperature of 105°C with an exposure of 2 minutes
5068.4	19725	ew, s	−1787	$0-538$ 1176 -2×37	
5059 2	19760	ow, s	−1752	$0-538$ 1176 -37	
5049.7	19798	ow, vs	−1714	$0-538$ - 1176	
5030.4	19874	ow, s	−1638	$0-3\times538-37$	
5020.6	19912	ow, s	−1600	$0-3\times538$	
5009 7	19956	w, d	−1556	$0-538$ 814 - 90 -3×37	
4998 2	20002	vw, d	−1510	$0-538-814-90-2\times37$	
4989.5	20037	vw, d	1475	$0-538-814-90-37$	
4980 9	20071	vw, d	1441	$0-538-814-90$	
4974 5	20097	vw, d	−1415	$0-538-814-64$	
4958 9	20160	m, s	1352	$0-538-814$ or $0-538-613-5\times37$ 12	The bands from 20160 cm^{-1} to 20910 cm^{-1} were measured and their intensities estimated from spectrograms at a temperature of 105 °C with an exposure of one minute.
4956 2	20171	w, s	−1341	$0-538-613-5\times37$ or $0+520-1680-3\times37$	
4949 5	20198	w, s	1314	$0-538-613-4\times37-12$	
4949 2	20208	w, s	−1304	$0-538$ 613 -4×37 or $0+520-1680-4\times37$	
4940.8	20234	w, s	−1278	$0-538-613-3\times37-12$	
4938 3	20244	w, s	−1268	$0-538-613-3\times37$ or $0+520-1680-3\times37$	
4931.6	20272	w, s	1240	$0-538-613-2\times37-12$	
4929 7	20280	w, s	1232	$0-538-613-2\times37$ or $0+510$ 1680 2×37	

TABLE I (Contd.)

Wavelength in Å	Wavenumbers in cm^{-1}	Intensity	Separation from (0,0)	Assignment	Remarks
4923 3	20306	w, sd	−1206	0−538−613−12	
4919.2	20323	w, sd	−1189	0−538−613−37 or 0+520−1680−37	
4914 8	20341	w, sd	−1171	0−538−613−12 or 0+520−1680	
4912.2	20352	w, sd	−1160	0−538−613 or 0+520−1674	
4904 4	20384	vw, sd	−1128	0+520−1680+36	
4902.7	20391	vw, sd	−1121		
4894 2	20427	w, vs	−1085	0+520−1680+2×36	
4889 4	20447	vw, sd	−1065		
4883.6	20471	vw, sd	−1041	0+520−1680+3×36	
4882.2	20477	vw, sd	−1035		
4868 0	20537	w, vs	− 975	0−538−291−4×37	
4864 6	20551	vw, sd	− 961		
4860.2	20570	vw, sd	− 942	0−538−291−3×37	
4855 9	20588	vw, sd	− 924		
4852 2	20603	vw, sd	− 909	0−538−291−2×37	
4847.2	20625	vw, sd	− 887		
4839.4	20658	vw, sd	− 854	0−538−291−37	
4833 6	20683	ms, sd	− 829	0−538−291	
4824 3	20723	ms, sd	− 789	0−538−291+36	
4822.5	20730	m sd	− 782	0−538−291+36+7	
4820.8	20738	w, sd	− 774		
4817 2	20753	w, sd	− 759	0−538−291+2×36	
4814 4	20765	w, sd	− 747		
4809.7	20786	w, sd	− 726	0−538−5×37 or 0+520+40−1680 or 0+520−2×613	
4807.6	20794	w, sd	718	0−538−2×90 or 0+520+440−1069	
4801.3	20822	w, sd	690		
4800.4	20826	bw, sd	686	0−538−4×37	
4793.6	20855	vw sd	657	0−538−3×37 or 0+520−1176	
4790.9	20867	m. s	645	0−538−37−64	
4784.9	20893	ms, s	619	0−538−90 or 0+520−1148	
4783.5	20899	m. s	613	0−613 or 0−538−2×37	
4781.1	20910	m, s	602	0−538−64	

TABLE I (*Contd.*)

Wavelength in Å	Wavenumbers in cm^{-1}	Intensity	Separation from (0,0)	Assignment	Remarks
4774 8	20937	vw, d		0−538−37	The bands from 20937 cm^{-1} to 21222 cm^{-1} develop even at 80°C. They are however measued and their intensities estimated from spectrograms taken at 105°C with exposure of two minutes.
4768.4	20966	w, vd	546	0−538−7	
4766.6	20974	vs, vs	538	0−538	
4760.4	21001	w, d	511	0−538+36−7	
4758 7	21008	vs, vs	504	0−538+36	
4755 9	21021	vw, d	491	0+520+1122−1149	
4750 2	21046	vs, vs	466	0−538+2×36	
4748 7	21053	m, s	459	0−538+2×36+7	
4747 5	21058	m, s	454	0−538+2×37+12	
4742.7	21079	m, s	433		
4741.1	21086	vs, vs	426	0−538+3×36	
4738.9	21096	m, s	416	0−538+3×36+12	
4733.6	21120		392	0−538−4×36	
4731 4	21130		382	0−538+4×36+12	
4726.5	21151		361	0−538−5×36 or 0+520+806−1680	
	21170		342	0−538−613+806 or 0+520+806−1667	
4718.5	21187	ms, s	325	0−538+6×36	
4710.9	21222	vw, s	290	0+520−814 or 0−291	
4707.3	21238	w, s	274	0+520−814	The bands from 21238 cm^{-1} to 22029 cm^{-1} are developed at 105°C. They are measured from spectrograms taken at 105°C with 1 minute exposure
4705 8	21245	w, s	267	0+520−814+7	
4704.9	21249	w, s	263	0+520−814+12	
4699 9	21271	vw, s	241	0+520−814+36	
4698.4	21278	vw, s	234	0+520−814+36+7	
4691 6	21309	vw, s	203	0+520−814+2×36	
4690 2	21315	vw, s	197	0+520−814+2+36+7	
4687.7	21327	vw, s	185		
4683.8	21344	vw, s	168	0+520−814+3×36	
4682.4	21351	vw, s	161	0+520−814+3×36+7	
4679.9	21362	vw, s	150	0+520−814+3×36+12	
4669 4	21410	ms, s		0−538+440	
4668.5	21414	w, s	98		
4667.8	21417	w, s	95	0−613+520	
4660.8	21450	vw, d	62	0−538+440+36	
4653.1	21485	m, s		0+520+1122−1667	
4651.1	21494	w, s	18		
4644.9	21524	m, d	12		
—	(21512)	—	0	0, 0	(Calculated)
4636.6	21562	w, d	50	0+520−470	
4630.3	21591	m, d	79	0+520−470+36	
4628.4	21599	w, ds			
4620.4	21637	w, sd	125	0+520−470+2×36	

TABLE I (*contd.*)

Wave-length in Å	Wave-numbers in cm^{-1}	Intensity	Separation from (0, 0)	Assignment	Remakrks
4614 1	21667	vw, sd	155	0+520−4×90	
4611.5	21678	vw, sd	166	0+520−470+3×36 or 0+520+440−794	
4602.9	21719	vw, sd	207		
4591 9	21771	ms, s	259	0−538+806	
4583.1	21813	w, s	301	0−538+806+36	
4575 8	21848	vw, d	336	0−538+806+36 0+520−2×90	
4571 9	21867	vw, d	355		
4568 8	21881	vw, d	369	0−538+806+3×36−7	
4567.7	21887	vw, d	375	0−538+806+3×36	
4562 9	21991	vw, sd	399		
4561.7	21916	vw, sd	404		
4560 5	21921	vw, sd	409	0−538+806+4×36 or 0+520−3×37	
4557.7	21935	w, d	423	0+520−90	The 21935 cm^{-1} band also develops at 80°C
4556.8	21939	ew, d	427		
4555 4	21945	we, s	433		
4552 7	21959	we, s	447	0+520−2×37	The 21980 cm^{-1} band also develops at 80°C
4550.1	21971	ew, s	459		
5448 3	21980	ms, s	468	0+520−64	
4546.1	21991	ew, s	479	0+520−3×18	
4543.3	22004	ms, s	492	0+520−37 or 0+520−2×18	
4541.4	22014	ms, s	502	0+520−18	
4539.2	22024	ms, s	512	0+520−7	
4538.3	22029	ew, s	517	0+520−3	
4537 6	22032	vs, vs	520	0+520	The bands from 22032 cm^{-1} to 22185 cm^{-1} develop even at 80°C. They are measured and then intensities estimated from plates taken at 85°C with 2 minute exposure.
4535 0	22042	vs, vs	530	0+520+12	
4533.4	22052	w, sd	540		
4530 7	22066	w, s	554	0+520+36−7	
4529 7	22070	s, s,	558	0+520+36	
4527.9	22079	vs, s	567	0+520+36+12	
4525 8	22089	w, s	577	0+574	
4523 1	22103	ms, s	591	0−538+1122	
4520 7	22114	s, s	602	0+520+2×36	
4518 7	22124	ms, s	612	0+520+2×36+12	
4515.7	22139	ew, s	627		
4513 4	22150	ms, s	638	0+520+3×36	
4511.0	22162	ms, s	650	0+520+3×36+12	
4508.2	22176	w, s	664		
4506.4	22185	ms, s	673	0+520+4×36	

TABLE I (*Contd.*)

Wavelength in Å	Wavenumbers in cm^{-1}	Intensity	Separation from (0,0)	Assignment	Remarks
4503 8	22197	vw. s	685		The bands from 22197cm^{-1} to 22458 cm^{-1} develop at 105°C. They are measured and their intensities estimated from spectrograms taken at 105°C with 3 minutes exposure
4501.4	22209	vw, s	697	0 + 520 + 5 × 36	
4499.2	22220	vw, s	708		
4495 5	22238	vw, s	726		
4491.8	22257	vw, s	745	0+520+227	
4490 3	22264	ew, s	752		
4487 2	22279	ew, s	767	0+520+1122 + 806−1688	
4484 9	22291	ew, ms	779	0+520+1122 + 806+1667	
4483.8	22296	ew, s	784		
4480.3	22314	ew, s	802		
4477.1	22330	ew, s	818		
4470.4	22363	ew, ms	851	0 + 520+440−3 × 37	
4465 3	22389	ew s	877	0 + 520 + 440−90	
4461 9	22406	ew, vs	894	0+ 520 +440−2 × 37	
4459.5	22418	ew, d	906	0 + 520+440−64	
4456 3	22434	ew, ms	922	0 + 520 + 440−37	
4451 5	22458	ew, ms	946	0 + 520 + 440−18	
4447 9	22476	ms, d	964	0 + 502 + 440	The bands from 22476 cm^{-1} to 22550 cm^{-1} develop at 80°C. The band at 22605 and 22700 cm^{-1} develop at 105°C
4441 8	22507	w, d	995	0+520+ 440 + 36	
4433 3	22550	w, d	1038	0 + 520+440 + 2 × 36	
4422 6	22605	vw, d	1094	0 + 520 + 2 × 806 or 0−538 + 1620	
4404 0	22700	w, sd	1188	0+ 520 + 1122−470	
4377 7	22837	ms, ms	1325	0 + 520+806	The bands from 22837 to 22945 cm^{-1} develop even at 80°C.
4370 9	22872	ms, ms	1360	0 + 520+ 806+ 36	
4363 8	22909	ms, ms	1397	0 +520+ 806 + 2 × 36 or 0 −538 + 1122+ 806	
4357 0	22045	ms, ms	1433	0 + 520+ 806+ 3 × 36	
4329 8	23089	w, sd	1577	0+ 520 + 1122−64	The band at 23089 cm^{-1} develops at 105°C. The bands from 23157 to 23269 cm^{-1} develop at 80°C. The bands from 23304 to 23528 cm^{-1} develop at 105°C.
4317.1	23157	s, sd	1645	0+ 520 + 1122	
4309 7	23196	m, sd	1684	0 + 520+1122 −35	
4303 2	23232	w, sd	1720	0+ 520+ 1122+ 2 × 36	
4296 3	23269	w, sd	1757	0+520+1122+ 3 × 36	
4290 0	23304	vw, sd	1792	0 +520 + 1122+4 × 36	
4282.4	23345	vw, sd	1833	0+ 520+ 1122 + 5 × 36	
4251.4	23515	m, sd	2003	0+ 520+ 1122+440−90	
4243 7	23528	w, sd	2016	0+520+1122+440−64	
4237.3	23593	ms, sd	2081	0+520+1122 +440	The bands from 23593 to 23751 cm^{-1} develop even at 80°C
4231 2	23627	m, sd	2115	0 + 520+1122 + 440+ 36 or 0+520+2 × 806	
4223 9	23668	m, sd	2156	0 + 520+ 1122 +440+ 2 × 36 or 0+520+ 1630	
4218 6	23708	w, sd	2196	0+ 520+1122+3 × 36	
4209.0	23751	vw sd	2259		

TABLE I (*Contd*)

Wavelengtl. in Å	Wavenumbers in cm^{-1}	Intensity	Separation from (0, 0)	Assignment	Remarks
4178 4	23926	m, sd	2414	0 + 520 + 1122 + 37	The bands at 23926 and from 24067 to 24520 cm^{-1} develop at 105°C The bands from 23955 to 24028 cm^{-1} develop even at 80°C
4173.4	23955	ms, sd	2443	0 + 520 + 1122 + 806	
4167.1	23991	m ,sd	2479	0 + 520 + 1122 + 806 + 36	
4160.7	24028	m ,sd	2516	0 + 520 + 1122 + 806 + 2 × 36	
4153 9	24067	w, sd	2555	0 + 520 + 1122 + 806 + 3 × 36	
4147.1	24106	vw, sd	2594	0 + 520 + 1122 + 806 + 4 × 36	
4117 4	24280	vw, ms	2768	0 + 520 + 2 × 1122	The bands from 22476 to 24520 cm^{-1} are measured from spectrograms taken at 85°C as well as 105°C
4111 3	24316	vw, sd	2794	0 + 520 + 2 × 1122 + 36	
4099 9	24384	vw, sd	2872	0 + 520 + 2 × 1122 + 3 × 36	
4087.7	24456	vw, sd	2944	0 + 520 + 2 × 1122 + 5 × 36	
4077 2	24520	ow, sd	3008		

The experimental data are presented in Table I. Here the wavelengths in air are listed in column 1 and the corresponding wavenumbers in vacuo converted by means of Keyser's Schwingungszahlen in column 2. The values are believed to be accurate to within 2 cm^{-1} for the sharper bands and 5 cm^{-1} for the broad bands Visually estimated intensities and the degree of diffuseness of band-heads are given in column 3 The notations used in this column have the same meanings as in part II of the series (Singh, 1957–58). Column 4 is used to record the wavenumber differences between each band and the calculated (0, 0) band at 21512 cm^{-1}. Assignments are given in column 5 and 6, and the conditions under which the bands reported here were measured, are given.

PRELIMANARY AND GENERAL ANALYSIS

It is assumed that the para-benzoquinone molecule has a symmetry represented by D_{2h}(Vh). In case the visible system of benzoquinone is identified with the 4900Å system of benzene, it has to be assigned to a symmetry allowed transition (Kasha, 1947) resulting from the reduction of symmetry from D_{6h} to D_{2h}. However, an attempt to analyse the bands as due to an allowed transition is met with two serious difficulties, namely, the unaccountability of an interval of 1058 cm^{-1} between the strongest groups of the band system and the anomaly in the intensity distribution. Thus, it is not possible to assign unambiguously the (0,0) band of the system either at 20974 cm^{-1} or at 22032 cm^{-1} which are the two strongest bands. On the other hand, both these difficulties disappear if the analysis is made on the assumption of a forbidden transition made allowed by excitation of a suitable non-totally symmetric vibration. Under this assumption, the (0,0) band should have negligible intensity while the (0,1) and (1,0) bands of a non-totally symmetric vibration should show up strongly.

An inspection of the gross-structure of the spectrum shows that the strong bands at 22032 cm^{-1} and 20974 cm^{-1} can be assigned to the excited and the ground state vibration respectively superimposed upon the forbidden (0,0) band. The fact that the band at 20974 cm^{-1} is weaker in intensity in comparison to that at 22032 cm^{-1} and that it gains in intensity as the temperature is increased also lends support to this assignment The interval 1058 cm^{-1} between these two bands should then correspond to the sum of the excited state and ground state frequencies of some non-totally symmetric vibration which makes the transition allowed. In the Raman spectrum (Kohlrausch *et al*, 1913 and Stammereich *et al*, 1952) there is a frequency 538 cm^{-1} (K.P.S.) reported as 540 cm^{-1} by Stammereich and Forneris and this is depolarised. By choosing 538 cm^{-1} as the frequency of this vibration which makes the transition allowed, the excited state frequency will then be 520 cm^{-1}, so that sum of the two frequencies may be equal to 1058 cm^{-1}. With those assumptions, the general analysis of the main bands is given in Table II.

TABLE II.

General analysis of the main groups

Group No.	Wave-numbers in cm^{-1}	Intensity	Separation from (0, 0)	Assignments
I	20974	(6)	−538	0−538
	21512	—	0	(0, 0) (Calculated)
II	22032	(10)	520	0+520
III	22476	(5)	964	0+520+440
IV	22837	(5)	1325	0+520+806
V	23157	(8)	1645	0+520+1122
VI	23593	(3)	2081	0+520+440
VII	23955	(3)	2443	0+520+1122+806

The detailed analysis of the band (vide Table I) on the basis of a forbidden transition will now be given.

DETAILED ANALYSIS AND DISCUSSION

The transition is made allowed by a non-totally symmetric vibration of 538 cm^{-1} and is in many respects similar to the 2600A bands of benzene in its gross-structure. Just as in the 2600 A system of benzene the benzoquinone visible system should not have a (0,0) band, but instead a (0,1) band of a non-totally symmetric vibration. A (1, 0) band of the same vibration should occur with much

weaker intensity. For reasons discussed later, it seems probable that any of the b_{1g}, b_{2g} or b_{3g} vibrations may be instrumental in making the transitions allowed. Of these vibrations, there is one belonging to b_{1g} class, there are three belonging to b_{3g} class. As in benzene, carbon vibrations are expected to be more effective. There is difficulty, however, in establishing these vibrations, because the vibrational frequencies in the ground state of benzoquinone and their assignments to various modes of vibrations are not definitely known. As is well-known, the 606 cm^{-1} frequency of benzene splits into an (a_g) and a (b_{2g}) vibration (Sponer, 1942). The 444 cm^{-1} frequency found in the Raman spectrum is identified with the (a_g) part of this split vibration whereas 540 cm^{-1} may be identified as the b_{2g} part of the same vibration.

Another totally symmetric vibration has a frequency of 806 cm^{-1} in the excited state, and is associated with some kind of ring vibration. It is identified with the 794 cm^{-1} frequency found in the Raman spectrum (Strammereich and Forneris, 1952) though in that case, it will be observed that excited state frequency is slightly more than the ground state frequency. It is interesting to note that the same ground state 794 cm^{-1} vibration is found here loaded on various other suitable vibrations and is thus corroborated.

The 1122 cm^{-1} frequency found in the excited state corresponds to the ground state frequency of 1149 cm^{-1} found in the Raman spectrum (Stammereich and Forneris, 1952). The same Raman frequency has been reported as 1178 cm^{-1} by Kohlrauch *et al* (1913). The present work confirms this frequency as 1149 cm^{-1} and not as 1178 cm^{-1}. There is progression of this vibration which also appears in combination with 440 cm^{-1} and 806 cm^{-1} in the excited state. The intensity of the band with 1122 cm^{-1} frequency superimposed upon the (0, 1) band at 22032 cm^{-1} is greater than the intensity of bands resulting from the superposition of 440 cm^{-1} and 806 cm^{-1} on the same (0, 1) band. Further, the frequencies of 440 cm^{-1} and 806 cm^{-1} are loaded with one quantum on this 1122 cm^{-1} frequency already superimposed on the (0, 1) band. Thus, the successive groups are assigned as $0+520$, $0+520+440$, $0+520+806$, $0+520+1122$, $0+520+1122+440$ and $0+529+1122+806$. There is a very weak band group developed at a temperature of 105°C which is assigned as $0+520+2\times1122$. It is to be marked that at higher temperatures, bands develop when the ground state vibration of frequency 1149 cm^{-1} corresponding to this excited state vibration of frequency 1122 cm^{-1} is excited in combination with various frequencies. This indicates a preferential excitement of this vibration both in the ground and excited states of the molecule.

There is a totally symmetric vibration of 90 cm^{-1} frequency reported in the Raman spectrum by Kohlrauch *et al* (1913) but not confirmed by Stammereich and Forneries (1952). It is curious enough that there are bands in the visible spectrum which may be interpreted with this vibration of 90 cm^{-1} but for which there is always an alternative interpretation which appears to be more reasonable.

Thus, the band assigned as 0—538—90 may be assigned as 0+520—1149. As bands develop invariably at higher temperatures where the ground state frequency of 1149 cm^{-1} is probably excited it is assumed that the latter assignment is correct. This is further supported by the excitation of this vibration at these temperatures in combination with other vibrations.

Another totally symmetric vibration reported in the Raman spectrum is 1674 cm^{-1} which has been reported as a doublet having frequencies 1667 and 1688 cm^{-1} (Strammereich and Forneris, 1952). In the vapour spectrum, there are bands which are assigned as due to the ground state vibrations of 1667 cm^{-1} and 1688 cm^{-1}. The excited state frequencies corresponding to these vibrations are found to be 1676 cm^{-1} and 1630 cm^{-1}, but as they fall within other band groups where interactions may take place, it is not possible to assign these values unambiguously. The other vibrations are 241 cm^{-1} and 613 cm^{-1} corresponding to the Raman frequencies of 243 cm^{-1} and 610 cm^{-1}.

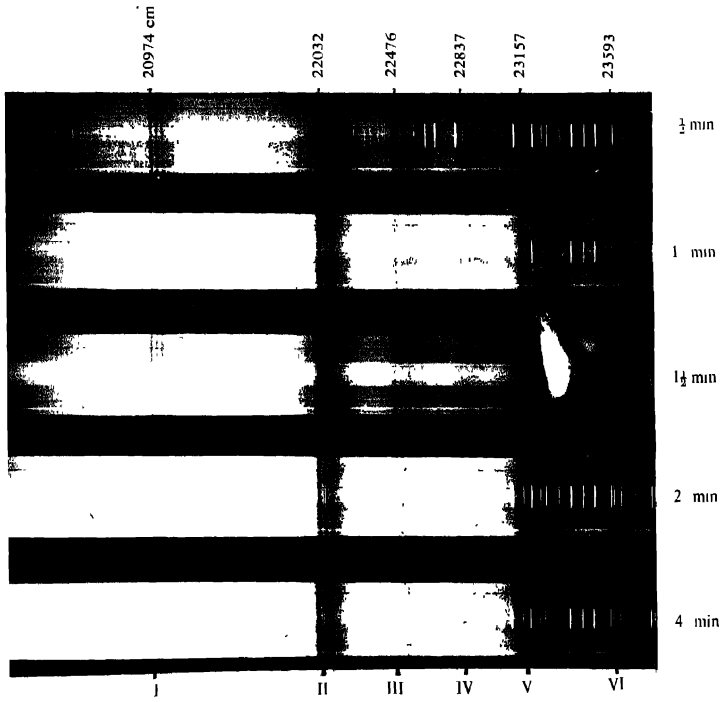
SYMMETRY TYPE OF THE EXCITED ELECTRONIC STATE

The ground electronic level of benzoquinone may be taken as A_g level. In order that it may be forbidden transition as it appears to be, the excited state should be either A_g or Au or B_{1g} or B_{2g} or B_{3g}. From the proposed analysis, this forbidden transition is made allowed by a Raman active 'g' vibration of frequency 538 cm^{-1}. Therefore, if a forbidden transition in D_{2h} symmetry is made allowed by a 'g' type of vibration, the excited electronic level must belong to 'u' type, as only this contains a translation. Thus, out of the five probable classes A_g, A_u, B_{1g}, B_{2g} and B_{3g}, the excited level must be (A_u). Therefore, this transition may be assigned as $A_u \leftarrow A_g$ on the basis of this analysis. This is in agreement with a theoretical calculation made by Sidman (1957).

It is interesting to note in this connection that the characteristic long wavelength absorption of carbonyl compounds has been interpreted by Mc. Murry as corresponding to a transition in which a loosely bound electron occupying a non-bonding orbital lying in the molecular plane and across CO direction is excited to an excited molecular orbital with a mode in the plane. On the basis of this, it was suggested that the visible absorption band of benzoquinone may also be of the same nature. Thus, this transition is assigned as $n \rightarrow \pi(A_u \leftarrow A_g)$ transition. As suggested by Kasha (1947), a decision as to the cause of prohibition in carbonyl bands would be of great interest. The present analysis reveals that the cause of prohibition is the 'forbiddenness' of the electronic transition rather than the intercombination.

OTHER FEATURES OF THE SPECTRUM

The 36 cm^{-1} recurring difference frequency lying on the shorter wavelength of each group may be interpreted as v, v transitions of two different vibrations



The visible absorption spectrum of benzoquinone at 100°C with different exposure times on a 3 prism Steinheil glass spectrograph

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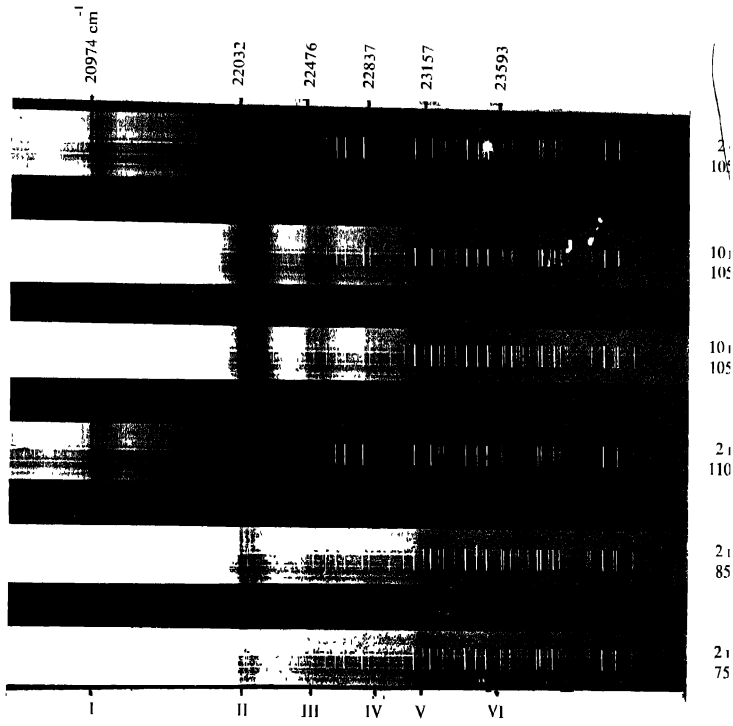
PLATE X



The visible absorption spectrum of benzoquinone with different exposures and at different temperatures.

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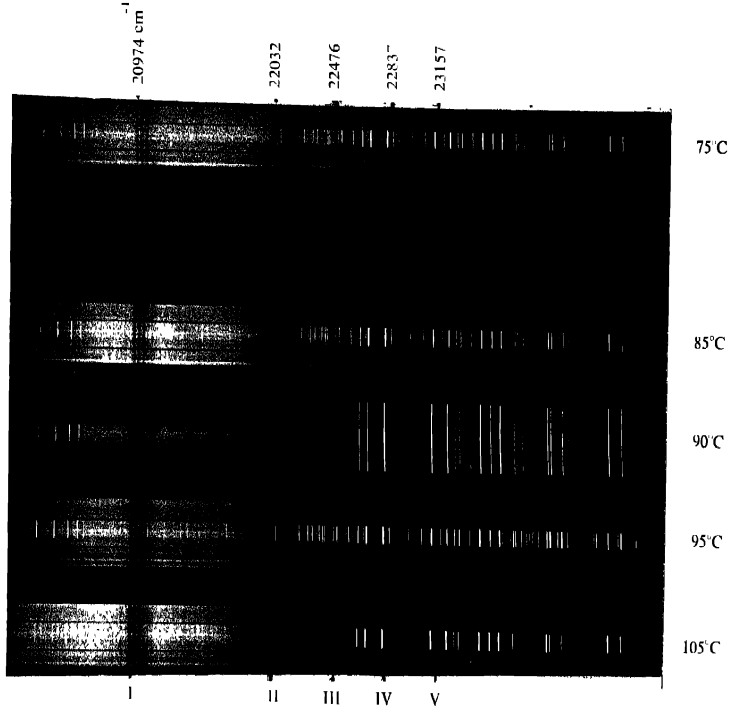
PLATE XI



The visible absorption spectrum at different temperatures and with the same exposure on the Steinheil glass spectrograph

possibly 538 cm^{-1} in the ground state and 574 cm^{-1} in the excited state, the latter corresponding to 613 cm^{-1} frequency in the ground state. Similarly, the v, v transitions of these two very vibrations with frequencies 520 cm^{-1} and 613 cm^{-1}, the former corresponding to 538 cm^{-1} in the ground state may be responsible for a recurring pattern of 90 cm^{-1}. The recurring pattern of 37 cm^{-1} on the longer wavelength side may likewise be assumed to be due to v, v transitions. Most of the bands are very sharp and have no degradations. However, there appears to be slight degradations towards violet in some of the bands. Many bands are double and triple headed, the common separations being 7 cm^{-1} and 5 cm^{-1} between triple-headed bands and 12 cm^{-1} between the double headed bands. The multiple heads may be due to rotational structure.

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